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(54) Title: INORGANIC PARTICULATE MATERIALS AND THEIR PRODUCTION

(57) Abstract

A method of producing a product inorganic particulate material which includes the steps of: (i) feeding to a particle size classifier a feed inorganic particulate material comprising kaolin which has a particle size distribution such that the percentage P by weight of particles having a size less than $x\mu$m, where $x\mu$m is repectively 2 μm, 1μm, 0.5μm, and 0.25 μm is as given in table 1; and (ii) separating the feed inorganic particulate material into a fine fraction and a coarse fraction, wherein at least the coarse fraction is extracted for use as a product inorganic particulate material.
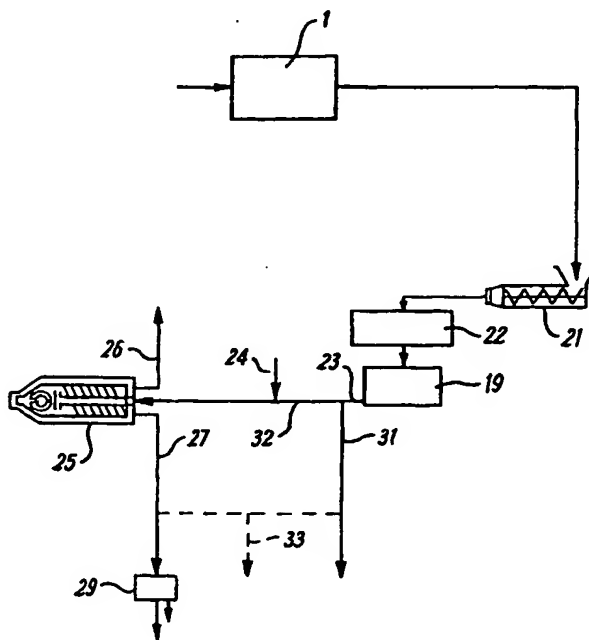
x (µm)	P (%)
2	at least 75
1	at least 55
0.5	at least 20
0.25	at least 10

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INORGANIC PARTICULATE MATERIALS AND THEIR PRODUCTION

The present invention relates to inorganic particulate materials and their production.

5   All printing processes require paper which is uniform in grammage, or weight per unit area, in calliper, or thickness, in moisture content, in water absorption and in formation, or texture. Papers for offset printing also need to be smooth and, if a coated

10   paper is used, the coating needs to adhere firmly to the base paper, so that fine pigment particles or fibres do not detach themselves from the paper and accumulate as dust or lint on the blanket. Also the paper must remain dimensionally stable in contact with

15   the aqueous fountain solution. The paper must also have a bright, white surface and generally a good gloss and must be sufficiently strong to run at high speeds through the printing machinery without damage.

A coating composition for a printing paper

20   generally consists of an aqueous suspension of one or more pigments and one or more adhesives or binders together with a dispersing agent for the pigment, and possibly one or more other additives. It is generally desirable for the composition to contain the minimum

25   amount of water which is consistent with adequate fluidity of the suspension, since the coated paper is generally dried by thermal energy, and energy efficiency is improved if the quantity of water to be removed by evaporation is kept to the minimum.

30   One of the pigments most commonly used in paper coating compositions comprises kaolin. Kaolin is a clay mineral, which is sometimes called china clay, and which was formed by the weathering of the feldspar

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component of granite. It is a hydrated aluminosilicate
which, in its natural form, consists of hexagonal,
plate-like crystals which may aggregate together to
form stacks of plates. When a printing paper which has
5   been coated with a composition containing kaolin is
calendered the plate-like crystals tend to orientate
themselves in the plane of the paper with the result
that the smoothness and gloss of the paper are
improved.
10   Paper manufacturers and printers are constantly
trying to improve the quality of their products, and
this makes it necessary for pigments having new and
improved properties to be used in the coating
compositions used to prepare the coated paper.
15   Various prior art publications describe processes
for treating kaolins to provide improvements in the
rheology of aqueous suspensions containing such
pigments. Examples include
GB-A-1,221,929, US-A-5,593,490 and "The Reduction of
20   Kaolin Slurry Viscosity using Pugging and Desliming" by
R A Lowe et al, Society for Mining, Metallurgy and
Exploration, Inc Annual Meeting, Orlando, Florida, 9-11
March 1998. Such references do not describe the effect
of such processes on optical or other properties in
25   coating compositions.
One purpose of the present invention is to provide
an inorganic particulate material comprising kaolin
which when used as a pigment or pigment ingredient in a
composition for coating paper or like material gives an
30   improved combination of coating properties including
brightness, eg brightness together with printability
and runnability.

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A further purpose of the invention includes the
production of fine kaolin products which can be used in
various specialist applications.

A further purpose of the invention is to provide a
5   method of producing various kaolin products having
desirable properties for use in selected applications.

According to the present invention in a first
aspect there is provided a method of producing one or
more product inorganic particulate materials comprising
10   kaolin which includes the steps of (i) feeding to a
particle size classifier a feed inorganic particulate
material comprising kaolin which has a particle size
distribution such that the percentage P by weight of
particles having a size less than xµm, where x is
15   respectively 2µm, 1µm, 0.5µm and 0.25µm, is as given in
the following table.

x (µm)	P (%)
2	at least 75
1	at least 55
0.5	at least 20
0.25	at least 10

and (ii) separating the feed inorganic particulate
20   material into a fine fraction and a coarse fraction.

The coarse fraction may comprise a product
inorganic particulate material having (optionally after
further processing) a particle size distribution such
that the percentage by weight P of particles having a
25   size less than xµm, where x is respectively 2µm, 1µm,
0.5µm and 0.25µm is as given in the following table:

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x (μm)	P (%)
2	at least 88
1	at least 60
0.5	at least 30
0.25	at least 10

A plot of P versus x is known as the particle size
distribution (psd) of the inorganic particulate
material. This plot and the individual values which
5   make up the plot may be measured by the well known
sedimentation technique of the particulate material in
a fully dispersed condition in an aqueous medium using
a SEDIGRAPH™ 5100 machine. Values of P for given
values of x and particle size distributions are
10   referred to herein are as measured in this conventional
manner. The particle size 50 measured is the
equivalent spherical diameter (esd).

Desirably, the inorganic particulate material of
the feed material consists of at least 90% by weight
15   kaolin, desirably at least 95% by weight kaolin.

The material produced as the coarse fraction and
that produced as the fine fraction may be further
processed, eg for beneficiation. The coarse fraction
may, for example, be treated by magnetic separation
20   and/or bleaching.

In the method according to the first aspect, the
feed inorganic particulate material may have a psd such
that $d_{50} \div d_{30}$ is greater than 1.57, eg greater than 1.60.
The $d_{50} \div d_{30}$ value of the coarse fraction may be at least
25   0.10 less than the $d_{50} \div d_{30}$ value of the feed material.

According to the present invention in a second
aspect there is provided an inorganic particulate
material comprising kaolin which has a particle size

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distribution such that the percentage P by weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm and 0.25µm is as given in the following table:

x (µm)	P(%)
2	at least 88
1	at least 60
0.5	at least 30
0.25	at least 10

Desirably, the product according to the first aspect has the following particle size properties:

x (µm)	P(%)
2	at least 89
1	at least 70
0.5	at least 35
0.25	10 to 20

The inorganic particulate material according to the second aspect of the present invention may consist of at least 90% by weight, desirably at least 95%, by weight kaolin.

A measure of the steepness of the psd of the inorganic particulate material according to the second aspect of the present invention may be given as the ratio $d_{50} \div d_{30}$ where d_{50} is the size value (in micrometres) smaller than which there are 50% by weight of the particles of the inorganic particulate material and d_{30} is the size value (in micrometres) smaller than which there are 30% by weight of the particles of the inorganic particulate material.

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Preferably, the inorganic particulate material according to the second aspect has a ratio $d_{50} \div d_{30}$ of less than 1.55, desirably not greater than 1.50. The ratio $d_{50} \div d_{30}$ may be in the range 1.35 to 1.50

5   especially 1.40 to 1.50.

Desirably, the d_{50} value of the psd of the inorganic particulate material according to the second aspect of the present invention is less than 2µm, preferably in the range 0.5µm to 1.5µm, more preferably

10   from 0.5µm to 1.0µm.

The inorganic particulate material according to the second aspect has a psd such that the material has a reduced content of fine particles together with a steep psd. By way of comparison, for example, a

15   commercially available product herein referred to as 'Kaolin 2' has the following particle size properties:

x (µm)	P (%)
2	93
1	76
0.5	51
0.25	24

but a d_{50}/d_{30} value of 1.61.

20   The reduced fines content and steep psd together with the selected d_{50} value of the inorganic particulate material according to the second aspect of the present invention beneficially allows better properties to be obtained when the material is used as

25   a pigment ingredient in a composition for coating paper and like sheet materials. In particular, a higher brightness and opacity, lower water retention giving improved porosity and ink absorptivity and improved

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composition rheology may be obtained as illustrated later.

The inorganic particulate material according to the second aspect of the invention may beneficially
5 have the following additional properties:

(i)   a powder brightness of at least 87, eg at least 89, and a powder yellowness of not more than 4.0. Powder brightness is defined as the percentage reflectance to light of wavelength 457nm as measured in
10 accordance with International Standard No ISO 2470 and powder yellowness is defined as the difference between the percentage reflectance of the powder to light of wavelength 457nm and the percentage reflectance to light of wavelength 570nm, both measured in accordance
15 with International Standard No ISO 2470;

(ii) a particulate shape factor of at least 10, eg in the range of from about 15 to about 30. Shape factor is defined as the average value (on a weight average basis) of the ratio of the mean particle diameter to
20 the particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity method and apparatus described in GB-A-2,240,398/US-A-5,128,606/EP-A-0,528,078 and using the equations derived in these patent specifications. If
25 the pigment in a paper coating composition has a high shape factor, this is an indication that the particles of the pigment are "platey" in nature. When paper coated with a composition containing such a pigment is subjected to calendering, the platey particles tend to
30 orientate themselves in the plane of the paper, with the result that the coated paper acquires a very desirable smoothness and gloss.

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According to a third aspect of the present invention there is provided an inorganic particulate material which is the fine fraction of the method according to the first aspect wherein the fine fraction

5   has a psd such that the percentage P by weight of particles having a size less than xμm, where x is respectively 2μm, 1μm, 0.5μm and 0.25μm is given in the following table.

x (μm)	P (%)
2	at least 95
1	at least 90
0.5	at least 50
0.25	at least 30

10

Desirably, the fine fraction has a psd defined by the following table.

x (μm)	P (%)
2	at least 98
1	at least 90
0.5	at least 60
0.25	at least 35

15   We have found that the fine fraction may itself advantageously be further classified into two sub-fractions. The first sub-fraction, which may be less fine than the second sub-fraction may have particle size properties as defined in the following table

20   (where x and P are as defined above).

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x (μm)	P (%)
2	greater than 95
1	greater than 90
0.5	less than 60
0.25	less than 20

Desirably, the said first sub-fraction has a psd as defined in the following table.

x (μm)	P (%)
2	at least 98
1	at least 90
0.5	less than 55
0.25	less than 15

In addition, the said first sub-fraction may have a $d_{50} \div d_{30}$ value of less than 1.55, desirably less than 1.50. The fine fraction which is classified into the first and second sub-fractions may have a $d_{50} \div d_{30}$ value of at least 1.60. Sub-classifying the fine fraction into the first and second sub-fractions may reduce the $d_{50} \div d_{30}$ value by at least 0.10, preferably by at least 0.15.

The material according to the second aspect of the present invention may be the coarse fraction product separated by the particle size classifier in the method according to the first aspect of the present invention. It may be blended with other coating pigment products, which may comprise kaolin and/or one or more of the coating pigments well known in the art, eg selected from ground or precipitated carbonates, eg calcium carbonate, calcined kaolin, talc, satin white, titanium

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dioxide, aluminium trihydrate, amorphous silicas and
silicates, zinc oxide, barium sulphate and so called
plastic pigments to form a coating pigment blend or
composition.

5   The coarse fraction product obtained by the method
according to the first aspect may beneficially be
blended in various ratios with the material employed as
the feed material in the method to produce by
separation in the particle size classifier the coarse
10   fraction product. The properties of the blend are
thereby intermediate between those of the coarse
fraction product and those of the feed material. The
properties of a coating pigment product may be tailored
by blending in this way as illustrated later. Although
15   it is known in the art to blend a fine fraction kaolin
product with a coarse fraction kaolin product it is not
known to blend a coarse fraction kaolin product with
the material employed as the feed material to produce
it.

20   In the method according to the second aspect, the
feed material may comprise an aqueous suspension of
inorganic particulate material comprising kaolin. The
classification device may comprise a centrifuge,
particularly a so-called decanter centrifuge, eg of the
25   so-called decanter scroll type. Such a device may
comprise a rotatable bowl and an independently
rotatable scroll inside the bowl, the feed material to
be classified being fed in aqueous slurry form to the
inside of the bowl in a region where it may be
30   influenced by the scroll. An example of a suitable
decanter centrifuge is described in EP 0,810,032. It
is well within the skill of the ordinary technician to
adjust the settings of the decanter centrifuge (or

other known particle size classifier if used) to obtain
a coarse fraction product having the properties
required of the material according to the first aspect
of the invention.

5   Where the fine fraction obtained by the method
according to the first aspect is itself sub-classified
as described earlier, the sub-classification may also
be carried out using a centrifuge, eg a decanter
centrifuge.

10   In the method according to the first aspect, the
feed material may comprise a product from a commercial
kaolin producing plant involving conventional
refinement and processing steps to give the appropriate
product properties, eg particle size distribution,

15   purity, whiteness, etc.   The product obtained from such
a plant may contain a chemical dispersing agent, such
as an organic polyelectrolyte, most frequently
comprising a polyacrylate salt.   Desirably, such a
product is diluted with water prior to use as a feed

20   material in the method according to the second aspect
thereby reducing the dispersing agent concentration in
the feed material and making classification of the
resulting diluted suspension, eg by decanter
centrifuge, easier.   In this case, the decanter

25   centrifuge will act as a re-concentrator and there may
not be a need for further dewatering of the coarse
fraction product.

         The fine fraction separated in the method
according to the first aspect may be used in one or

30   more ways which are known, eg by calcining to produce a
calcined kaolin pigment or by aggregation by
entrainment with precipitated bonding agent in the
manner described in EP 0,604,095.   Alternatively, or in

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addition, the fine fraction may be blended with either
or both of the feed material and the coarse fraction
product to provide a pigment blend. In this case, sub-
classification of the fine fraction into the first and
5   second sub-fractions described earlier may assist in
the design of the blend properties. For example,
addition of the steep psd first sub-fraction to the
steep psd coarse product will give overall a steep psd
blend.

10   An example of a form of the method according to
the first aspect of the present invention, herein
called the 'Method Form' may comprise the following
steps:

(a)   forming a concentrated aqueous suspension of an
15   intermediate kaolin clay product having a particle size
distribution such that at least about 75% by weight
consists of particles having an equivalent spherical
diameter smaller than 1μm, and a percentage reflectance
to light of wavelength 457nm of at least 87, as
20   measured in accordance with International Standard No
ISO 2470, in an aqueous medium in an undispersed state,
the solids content of the suspension being at least 60%
by weight;

(b)   subjecting the concentrated suspension formed in
25   step (a) to mechanical working in the plastic state
under conditions such that at least 215kJ of energy per
kg of kaolin clay on a dry weight basis are dissipated
in the suspension;

(c)   optionally grinding the solids material of the
30   suspension by a media attrition grinding process;

(d)   converting the concentrated suspension worked in
step (b) into a fluid aqueous suspension by a procedure

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involving diluting with water to produce a diluted
suspension;

(e)   subjecting the diluted suspension formed in step
(d) to fractionation in a centrifuge to yield a
5   relatively fine fraction and a relatively coarse
fraction under conditions such that it is exposed to an
acceleration which is in the range of from 1600g to
6000g, where g is the acceleration due to gravity; and
(f)   recovering the relatively coarse product as a
10   dispersed aqueous suspension.

The recovered coarse product may for example have
a solids concentration of at least 60% by weight, eg
from 65% to 78% by weight, the solid component
consisting of a refined kaolin clay having a particle
15   size distribution such that at least 75% by weight
consists of particles having an equivalent spherical
diameter smaller than 2µm, from about 45% to about 60%
by weight consists of particles having an equivalent
spherical diameter smaller than 1µm and not more than
20   10% by weight consists of particles having an
equivalent spherical diameter smaller than 0.25µm and,
as a dry powder, a percentage reflectance to light of
wavelength 457nm of at least 83, as measured in
accordance with International Standard No ISO 2470.

25   In step (a) of the Method Form the intermediate
kaolin clay product is preferably prepared from an
English crude kaolin deposit as clay products prepared
from such sources generally have a desirably high shape
factor as defined earlier. The intermediate kaolin
30   clay product employed in step (a) may be prepared by a
known process involving steps providing refinement and
beneficiation. The process may involve one or more of

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particle size classification, comminution, degritting, bleaching and dewatering.

The suspension provided in step (a) may be dewatered to the required concentration by pressure

5   filtration, although other means, such as a centrifuge, might alternatively be used to give such concentration. The suspension is preferably dewatered to a solids content greater than 70% by weight, eg in the range of from 73% to 77% by weight.

10   In step (b) above the concentrated suspension formed in step (a) is preferably subjected to mechanical working in a pugmill, although other devices such as a muller, kneader or Z-blade mixer may also be used. The amount of energy dissipated in the

15   concentrated suspension during the mechanical working is preferably in the range of from 215kJ to 430kJ, and more preferably from 290kJ to 395kJ per kg of kaolin on a dry weight basis. The purpose of the working is to provide a suspension free of lumps which can be

20   suitably dispersed or further treated as a collection of individual fine particles.

In optional step (c), the suspension may be media attrition ground in a known manner, to give a particle size distribution such that at least 80%, in some cases

25   at least 90%, by weight has a particle size less than 2µm and at least 15%, desirably at least 20%, eg 20% to 30%, has a particle size less than 0.25µm.

The kaolin employed in step (a) may itself be employed as the basis of a kaolin product for use in or

30   as a pigment for coating compositions as well as providing a feed material in the method according to the second aspect of the present invention. In this case, a conventional dispersing agent may be added to

the concentrated suspension to allow a high solids
fluid slurry product to be formed. The product of step
(b) may be diluted with water in step (d) to provide a
suitable suspension of feed material for centrifugation
5   in the method according to the second aspect of the
present invention. Where a dispersing agent has been
added prior to the dilution, the dilution will render
the suspension more suitable for treatment by the
centrifuge.

10   In step (e) above the centrifuge is preferably of
the scroll decanter type as described earlier, and is
preferably operated under conditions such that the feed
suspension is subjected to an acceleration in the range
of from 1800g to 2100g, where g is the acceleration due
15   to gravity.

In step (f) above, the relatively fine fraction as
well as the coarse fraction obtained from fractionation
by the centrifuge may be recovered as a valuable kaolin
product. The relatively fine fraction will typically
20   have a particle size distribution such that about 95%
to about 100% by weight consists of particles having an
equivalent spherical diameter smaller than 2µm, about
90% to about 100% by weight consists of particles
having an equivalent spherical diameter smaller than
25   1µm, about 60% to about 75% by weight consists of
particles smaller than 0.5µm and from about 25% to
about 65% by weight consists of particles smaller than
0.25µm. This very fine kaolin product may be used
optionally after further processing, eg after further
30   particle size classification, in one of the ways
described earlier or as a fine pigment or filler in
other applications, eg as reinforcing filler for rubber

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and plastics (wherein good rigidity, abrasion
resistance and low particle surface area are provided).

The fine sub-fraction if required may need to be
concentrated by dewatering. The concentration may be
5   carried out in a known manner, eg by membrane
filtration, eg cross-flow membrane filtration.

Where a dispersing agent is employed in the Method
Form, eg steps (a) and (b), the dispersing agent may be
a water soluble salt of a polycarboxylic acid, such as
10 a water soluble salt of a poly(acrylic acid), of a
poly(methacrylic acid) or of a poly(maleic acid), or of
a copolymer of two or more of maleic acid, acrylic acid
or methacrylic acid. The water soluble polycarboxylate
preferably has a weight average molecular weight in the
15 range of from about 1500 to about 10,000. Sodium or
ammonium polycarboxylates are most preferred. The
amount of the dispersing agent used is preferably in
the range of from about 0.05% to about 1.0% by weight,
based on the dry weight of kaolin.

20   In dilution step (d) of the Method Form the
aqueous suspension is preferably diluted with from 4 to
6 times its own weight of water having an electrical
conductivity not greater than 300µS, which may
conveniently be purified water drawn from the municipal
25 mains.

According to the present invention in a fourth
aspect there is provided a paper coating composition
for preparing a coated printing paper, which is
especially suitable for offset lithography printing,
30 which composition comprises an aqueous suspension of a
pigment or mixture of pigments, together with a
hydrophilic adhesive or binder, the pigment or pigments

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comprising inorganic particulate material according to
the first aspect.

The sheet material to which the coating
composition according to the third aspect is to be

5   applied may be any of the materials known to be treated
with a water based coating composition comprising
coating pigment and adhesive and other optional
ingredients. Such sheet material may comprise any of
the sheet materials commercially coated with such a

10   composition, eg paper, paper board, card, cardboard and
like products made from cellulosic and/or synthetic
fibre compositions.

The aqueous coating composition according to the
fourth aspect is desirably substantially free of

15   volatile organic solvents. The aqueous coating
composition may include together with pigment material
comprising inorganic particulate according to the first
aspect of the invention any one or more of the pigment
materials known or used in the art, eg as described

20   earlier.

Coating compositions for use in coating sheet
materials vary depending upon the materials to be
coated which vary throughout the world depending upon
the geography of the region in which the material is

25   produced as well as the intended use of the sheet
material. The compositions according to the third
aspect are especially beneficial to produce paper and
other sheet materials suitable for printing by offset
lithography.

30   The coating composition according to the third
aspect may include as adhesive or binder, depending on
the type of composition concerned, any one or more of
the hydrophilic adhesives known or used in the art, eg

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selected from starches and other polysaccharides,
proteinaceous adhesives, and latices.

The amount of adhesive or binder present in the
composition depends upon whether the composition is to
be applied as a relatively dilute or concentrated
pigment-containing suspension to the material to be
coated. For example, a dilute pigment-containing
composition (binder-rich composition) could be employed
as a top-coat for underlying more pigment-rich
compositions. The adhesive or binder present in the
composition may range from 1% to 70% by weight relative
to the dry weight of pigment (100% by weight)
especially 4% to 50% by weight. Where coating
composition is not to be employed as a binder rich
composition the adhesive or binder may form from 4% to
30%, eg 8% to 20%, especially 8% to 15% by weight of
the solids content of the composition. The amount
employed will depend upon the composition and the type
of adhesive, which may itself incorporate one or more
ingredients. For example, the following adhesive or
binder ingredients may be used in the following stated
amounts:

(a) **Latex**: levels range from 4% by weight for self
thickening gravure latices to 20% by weight for board
coating latices. The latex may comprise for example a
styrene butadiene, acrylic latex, vinyl acetate latex,
or styrene acrylic copolymers.

(b) **Starch and other binders**: levels range from 0 to
50% by weight, eg 4% by weight to 20% by weight for
pigment-rich compositions. The starch may comprise
material derived from maize, corn and potato. Examples
of other binders include casein and polyvinyl alcohol.

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Additives in various known classes may, depending upon the type of coating and material to be coated, be included in the coating composition to be concentrated by the method according to the present invention.

5   Examples of such classes of optional additive are as follows:

(a)   **Cross linkers**: eg in levels 0 to 5% by weight; for example glyoxals, melamine formaldehyde resins, ammonium zirconium carbonates.

10   (b)   **Water retention aids**: eg in up to 2% by weight, for example sodium carboxymethyl cellulose, hydroxyethyl cellulose, PVA (polyvinyl acetate), starches, proteins, polyacrylates, gums, alginates, polyacrylamide bentonite and other commercially

15   available products sold for such applications.

(c)   **Viscosity modifiers or thickeners**: eg in levels up to 2% by weight; for example polyacrylates, emulsion copolymers, dicyanamide, triols, polyoxyethylene ether, urea, sulphated castor oil, polyvinyl pyrrolidone,

20   montmorillonite, CMC (carboxymethyl celluloses), sodium alginate, xanthan gum, sodium silicate, acrylic acid copolymers, HMC (hydroxymethyl celluloses), HEC (hydroxyethyl celluloses) and others.

(d)   **Lubricity/Calendering aids**: eg in levels up to 2%

25   by weight, for example calcium stearate, ammonium stearate, zinc stearate, wax emulsions, waxes, alkyl ketene dimer, glycols.

(e)   **Dispersants**: eg in levels up to 2 per cent by weight, for example polyelectrolytes such as

30   polyacrylates (sodium and ammonium), sodium hexametaphosphates, non-ionic polyol, polyphosphoric acid, condensed sodium phosphate, non-ionic

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surfactants, alkanolamine and other reagents commonly
used for this function.

(f)   Antifoamers/defoamers: eg in levels up to 1% by
weight, for example blends of surfactants, tributyl

5   phosphate, fatty polyoxyethylene esters plus fatty
alcohols, fatty acid soaps, silicone emulsions and
other silicone containing compositions, waxes and
inorganic particulates in mineral oil, blends of
emulsified hydrocarbons and other compounds sold

10   commercially to carry out this function.

(g)   Dry or wet pick improvement additives: eg in
levels up to 2% by weight, for example melamine resin,
polyethylene emulsions, urea formaldehyde, melamine
formaldehyde, polyamide, calcium stearate, styrene

15   maleic anhydride and others.

**(h)   Dry or wet rub improvement and abrasion resistance
additives**: eg in levels up to 2% by weight, for example
glyoxal based resins, oxidised polyethylenes, melamine
resins, urea formaldehyde, melamine formaldehyde,

20   polyethylene wax, calcium stearate and others.

(i)   Gloss-ink hold-out additives: eg in levels up to
2% by weight, for example oxidised polyethylenes,
polyethylene emulsions, waxes, casein, guar gum, CMC,
HMC, calcium stearate, ammonium stearate, sodium

25   alginate and others.

**(j)   Optical brightening agents (OBA) and fluorescent
whitening agents (FWA)**: eg in levels up to 1% by
weight, for example stilbene derivatives.

(k)   Dyes: eg in levels up to 0.5% by weight.

30   **(l)   Biocides/spoilage control agents**: eg in levels up
to 1% by weight, for example metaborate, sodium
dodecylbenene sulphonate, thiocyanate, organosulphur,
sodium benzonate and other compounds sold commercially

for this function eg the range of biocide polymers sold by Calgon Corporation.

(m)   Levelling and evening aids: eg in levels up to 2% by weight, for example non-ionic polyol, polyethylene emulsions, fatty acid, esters and alcohol derivatives, alcohol/ethylene oxide, sodium CMC, HEC, alginates, calcium stearate and other compounds sold commercially for this function.

(n)   Grease and oil resistance additives: eg in levels up to 2% by weight, eg oxidised polyethylenes, latex, SMA (styrene maleic anhydride), polyamide, waxes, alginate, protein, CMC, HMC.

(o)   Water resistance additives: eg in levels up to 2% by weight, eg oxidised polyethylenes, ketone resin, anionic latex, polyurethane, SMA, glyoxal, melamine resin, urea formaldehyde, melamine formaldehyde, polyamide, glyoxals, stearates and other materials commercially available for this function.

(p)   Insolubiliser: eg in levels up to 2% by weight.

For all of the above additives, the percentages by weight quoted are based on the dry weight of pigment (100%) present in the composition. Where the additive is present in a minimum amount the minimum amount may be 0.01% by weight based on the dry weight of pigment.

Methods of coating paper and other sheet materials are widely published and well known. For example, there is a review of such methods published in Pulp and Paper International, May 1994, page 18 et seq. Sheets may be coated on the sheet forming machine, ie "on-machine", or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water to evaporate subsequently. However, as is well known in

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the art, the solids level should not be so high that high viscosity and levelling problems are introduced.

All known methods of coating for use in step (b) of the method according to the present invention require (i) a means of applying the coating composition to the material to be coated, viz an applicator; and (ii) a means for ensuring that a correct level of coating composition is applied, viz a metering device. When an excess of coating composition is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating composition may be applied to the applicator by the metering device, eg as a film press. At the points of coating application and metering, the paper web support ranges from a backing roll, eg via one or two applicators, to nothing (ie: just tension). The time the coating is in contact with the paper before the excess is finally removed is the dwell time - and this may be short, long or variable.

The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single coated, double coated and even triple coated. When providing more than one coat, the initial coat (precoat) may have a cheaper formulation. A coater that is applying a double coating, ie a coating on each side of the paper, will have two or four coating heads, depending on the number of sides coated by each head. Most coating heads coat only one side at a time, but some roll coaters (eg film press, gate roll, size press) coat both sides in one pass.

Examples of known coaters which may be employed in coating of a sheet material using a composition

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according to the third aspect of the invention include
air knife coaters, blade coaters, rod coaters, bar
coaters, multi-head coaters, roll coaters, roll/blade
coaters, cast coaters, laboratory coaters, gravure

5   coaters, kiss coaters, liquid application systems,
reverse roll coaters and extrusion coaters.

      Embodiments of the present invention will now be
described by way of example with reference to the
accompanying drawing and the Examples which follow

10   later. In the accompanying drawing Figure 1 is a
diagrammatic flow sheet of a process embodying the
invention for the treatment of an aqueous kaolin
suspension.

      As shown in Figure 1, a starting kaolin product

15   having a particle size distribution such that at least
75% by weight consists of particles having an
equivalent spherical diameter smaller than 2µm and is
in the form of an aqueous suspension having a solids
concentration (the kaolin) of from 15% to 30% by

20   weight. The suspension is passed through a series 1 of
conventional processing stages involving one or more of
particle size classification, comminution, degritting,
bleaching and dewatering to produce a high solids
suspension or cake, eg having a solids content greater

25   than 50% by weight, desirably greater than 60% by
weight, which forms the input to a pugmill 21. The
cake is subjected to mechanical working in the pugmill
21 under conditions such that at least 215kJ, eg about
325kJ, of energy are dissipated in the cake per

30   kilogram of kaolin on a dry weight basis. The
mechanically worked cake is then transferred to a
liquid mixer 22, where a sodium polyacrylate dispersing
agent is added, and is well mixed with the cake to form

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a fluid dispersed suspension of the treated kaolin.
This fluid suspension is then fed to a grinding machine
19 wherein the suspension is media attrition ground in
a known manner to give a particle size distribution

5   such that at least 80%, preferably at least 90%, by
weight of the particles are smaller than 2μm and >15%,
preferably from 20% to 30% by weight are smaller than
0.25μm. The ground suspension is pumped through a
conduit 23 where it is split into two streams 31 and

10   32. The first stream 31 may be stored in a storage
vessel (not shown) and then pumped and transported in a
conventional manner and used in its own right as a
dispersed pigment slurry for the production of coating
compositions. The product produced in this way is

15   Kaolin 2 described earlier which is a commercially
available product having the properties specified
earlier.

The second output stream 32 from the liquid mixer
22 is diluted with five times its own weight of

20   municipal mains water, which is supplied through a
conduit 24, to a solids concentration of about 21% by
weight. The diluted suspension is fed to a scroll-type
decanter centrifuge 25, which is operated under
conditions such that it provides an acceleration in the

25   range of from 1800g to 2100g, and in which the
suspension is fractionated into a relatively fine
fraction which is discharged over the overflow weirs of
the centrifuge through a conduit 26, and a relatively
coarse fraction which is conveyed by the scroll of the

30   centrifuge 25 to one end of the centrifuge bowl, whence
it is discharged through a conduit 27.

The relatively fine fraction produced by the
centrifuge 25 consists of a suspension of a very fine

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kaolin product which has a particle size distribution
such that about 95% to about 100% by weight consists of
particles having an equivalent spherical diameter
smaller than 2μm, about 90% to 100% consists of
5   particles smaller than 1μm and from about 25% to about
65% by weight consists of particles smaller than
0.25μm. This very fine product may be recovered and
employed in one of a variety of possible applications,
eg as a filler for rubber or plastics compositions, or
10 as a feed material for producing fine calcined kaolin,
or may be blended with other kaolin products for
preparing paper coating pigments, eg it may provide a
fine glossing pigment component. The fine fraction may
be further fractionated before use, eg as described
15 earlier using a further decanter centrifuge 29. The
resulting fine sub-fraction may be employed as a
retention aid in paper making together with a water
soluble flocculant polymer in a known manner. The
resulting relatively coarse sub-fraction (which is the
20 coarser of two very fine sub-fractions) may be employed
as a fine glossing pigment, eg as a fine component of
pigment compositions for use in gloss coatings for
paper, board and the like. This coarse sub-fraction
may also find beneficial use as a fine particulate
25 filler, extender or property modifier in non-paper
applications, eg in polymeric or rubber compositions
(eg from 5% to 60% by weight of the composition). This
product may have an unusual combination of properties,
eg a low relative specific surface area for its
30 particle size distribution beneficial in such
applications. For example, these properties may give
enhanced rigidity and abrasion resistance in the
compositions to which the product (ie the coarse sub-

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fraction) is added. For instance, the specific surface area may be less than $40m^2.g^{-1}$, eg less than $30m^2.g^{-1}$, especially $20m^2.g^{-1}$ to $30m^2.g^{-1}$. The psd may be as defined by the following table, where x and P are as
5   defined earlier.

x (μm)	P (%)
2	at least 98
1	at least 90
0.5	30 to 60

The relatively coarse fraction produced by the centrifuge 25 is found to consist of a suspension
10   containing at least 65% by weight of a kaolin product which requires no further dewatering and has very desirable properties when incorporated in a coating composition especially for preparing coated papers for printing, eg by offset lithography.
15   The relative coarse fraction delivered via the conduit 27 and the product Kaolin 2 delivered via the stream 31 may be blended in various proportions in a blend stream 33.

The following Examples exemplify the production of
20   kaolin products embodying the invention using the process illustrated in Figure 1.

EXAMPLE 1

A refined kaolin product prepared by the process
25   described with reference to Figure 1 was found to have a particle size distribution such that 86% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm, 56% by weight consisted of particles having an equivalent spherical diameter

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smaller than 1µm, 21% by weight consisted of particles
smaller than 0.5µm and 5% by weight consisted of
particles smaller than 0.25µm. The shape factor, as
defined above, was 19. The percentage reflectance to
5   light of 457nm wavelength shown by the dry kaolin
powder was 89.5. This kaolin product is referred to in
the description of an experiment which follows as
"Kaolin 1".

A kaolin product which is representative of those
10   which are currently being marketed as the best
available for use as a pigment in a coating composition
for preparing coated papers for offset lithography
printing is Kaolin 2 referred to earlier (having the
particle size properties given earlier). The shape
15   factor of Kaolin 2 was measured as 23. The percentage
reflectance to light of 457nm wavelength shown by the
dry kaolin powder Kaolin 2 was found to be 89.0.

Paper coating compositions for producing coated
printing papers for offset lithography were prepared
20   containing, as the pigment, either 100% by weight of
Kaolin 1 or Kaolin 2, or one of a series of blends of
these two kaolin products in different proportions by
weight.

In each case the paper coating composition had the
25   following formulation:

Ingredient	Parts by weight
Pigment	100
Synthetic latex binder	7
Optical brightening agent	0.3
Sodium carboxymethyl cellulose	0.3
Sodium hydroxide	to pH 7.5

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The water content of each composition was adjusted
to be the minimum amount consistent with sufficient
fluidity to enable the composition to be usable in the
paper coating machine. The percentage by weight of
5   water in each composition was measured by drying and
weighing a sample of known weight of the composition,
and the low shear viscosity of each composition was
measured at 22°C using a Brookfield Viscometer at a
spindle speed of 100rpm.

10   The water release and retention of each
composition was measured by the method described in the
paper "Measuring the water retention of coating colors"
by Stefan E Sandas, Pekka J Salminen and Dan E Eklund,
TAPPI Journal, Vol 72, No 12, December 1989, pages 207-
15   210. This method is based on pressure filtration and
involves the gravimetric determination of the amount of
the aqueous phase of a composition which penetrates in
a given time under a given hydrostatic pressure through
a hydrophilic polycarbonate filter of pore size 5μm
20   into an absorbent paper. In each case the pressure
applied was 1.0bar and the contact time was 30s.

Each composition was coated onto an offset base
paper of substance weight 41g.m^{-2} on a paper coating
machine of the type described in GB-A-1032536 operating
25   at a paper speed of 1000m.min^{-1}. Samples of each
composition were coated at a series of different blade
pressures to give different weights per unit area on
the paper web. Each sample of paper was calendered
before testing by being passed 8 times through the nip
30   of a supercalender at a temperature of 65°C and a line
pressure of 89.3 kg.cm^{-1}. Measurements of the paper
properties described below were made on a sample of
coated paper at each coat weight and, for each

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property, the value of the property which corresponded to a coat weight of $10g.m^{-2}$ was found by interpolation.

The following properties of the samples of coated paper were measured:

5   The percentage reflectance of samples of the coated paper to light of 457nm and 570nm wavelength was measured by means of a DATACOLOR "ELREPHO" 3000 spectrophotometer ("DATACOLOR" and "ELREPHO" are trade marks) fitted with a xenon light source which emits

10   light rich in radiation of wavelength in the ultraviolet range.

Samples of coated paper from each batch were tested for opacity by means of a DATACOLOR "ELREPHO" 3000™ spectrophotometer set to embrace a broad spectrum

15   of wavelengths. A measurement of the percentage of the incident light reflected was made with a stack of ten sheets of paper over the black cavity of the brightness meter (R_∞). Of these ten sheets, the top five were from the sample of paper currently under test, and the

20   remaining five were sheets from other samples which were used merely to ensure that the stack was completely opaque. The ten sheets were then replaced with the single sheet from the top of the stack of five test sample sheets over the black cavity and a further

25   measurement of the percentage reflectance was made (R). The percentage opacity was calculated from the formula:

Percentage opacity = $100.R/R_\infty$

The procedure was performed five times with each time a different sheet of paper on top of the stack,

30   and the complete sequence of steps was then repeated to give a total of ten results from which the average value of the percentage opacity was determined.

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The results obtained are set forth in Table 1 below:

TABLE 1

Wt. ratio Kaolin 1: Kaolin 2	% by wt. solids in composition	Viscosity of composition (mPa.s)	Water release (g.m^{-2})	% reflectance to light of wavelength		Opacity (%)
				457nm	570nm	
0:100	59.7	660	50	76.0	78.9	88.9
25:75	60.9	560	53	76.9	79.5	89.6
50:50	60.9	400	60	77.2	79.8	89.5
75:25	61.1	310	72	77.5	80.2	89.6
100:0	61.2	200	95	78.2	80.7	90.1

5

These results show that Kaolin 1, the product embodying the invention, when incorporated into a typical coating composition for preparing a coated printing paper for offset lithography, gives a

10 composition which is sufficiently fluid for use on a paper coating machine which at the same time has a higher solids concentration and a lower viscosity than Kaolin 2, which is currently marketed as a good quality pigment for preparing coating compositions for offset

15 printing papers. Kaolin 1 provides a coating composition which shows significantly higher water release and therefore lower water retention than does Kaolin 2. A composition of low water retention leads to a more porous coated paper, and in many cases this

20 is considered to be a desirable property because the ink absorptivity of the paper is increased. Kaolin 1 also provides a coated paper which has a higher brightness, as evidenced by the percentage reflectance to light of wavelength 457nm, and a lower "yellowness",

25 which is given by the difference between the percentage reflectance to light of 570nm wavelength and the

percentage reflectance to light of wavelength 457nm, than Kaolin 2. Kaolin 1 also provides coated papers of higher opacity than Kaolin 2.

Coated papers having properties intermediate between those given by Kaolin 1 and those given by Kaolin 2 may be obtained by blending the two pigments in any desired proportion. Generally at least 25% by weight of Kaolin 1 in the mixture is desirable to provide a significant benefit.

EXAMPLE 2

A further example of a product embodying the invention and made using Kaolin 2 as feed material by the process illustrated in Figure 1 was found (prior to drying) to have the following properties (where x and P are as defined earlier).

x (μm)	P (%)
2	89
1	64
0.5	33
0.25	14

The product showed similar benefits and could be blended with Kaolin 2 in a similar manner to Kaolin 1 in Example 1.

EXAMPLE 3

A further example of a product embodying the invention and made using Kaolin 2 as feed material process illustrated in Figure 1 was found (prior to drying) to have the following properties (where x and P are as defined earlier).

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x (µm)	P (%)
2	90
1	70
0.5	37
0.25	10

together with d_{50} = 0.66µm, d_{30} = 0.45µm and $d_{50} \div d_{30}$ = 1.46

EXAMPLE 4

A further example of a product embodying the invention and made using Kaolin 2 as feed material process illustrated in Figure 1 was found following pressing and drying to a powder to have the following properties (where x and P are as defined earlier).

x (µm)	P (%)
2	91
1	72
0.5	40
0.25	13

together with d_{50} = 0.6, d_{30} = 0.4 and $d_{50} \div d_{30}$ = 1.5.

EXAMPLE 5

A further example of a product embodying the invention and made using Kaolin 2 as feed material process illustrated in Figure 1 was found following pressing and drying to a powder to have the following properties (where x and P are as defined earlier).

x (μm)	P (%)
2	90
1	70
0.5	38
0.25	15

together with $d_{50} = 0.64$, $d_{30} = 0.41$ and $d_{50} \div d_{30} = 1.56$.

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CLAIMS

1.   A method of producing a product inorganic particulate material which includes the steps of (i)
5   feeding to a particle size classifier a feed inorganic particulate material comprising kaolin which has a particle size distribution such that the percentage P by weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm, and 0.25µm is
10   as given in the following table.

x (µm)	P (%)
2	at least 75
1	at least 55
0.5	at least 20
0.25	at least 10

and (ii) separating the feed inorganic particulate material into a fine fraction and a coarse fraction,
15   wherein at least the coarse fraction is extracted for use as a product inorganic particulate material.

2.   A method according to claim 1 and wherein the said coarse fraction, optionally after further processing, has particle size distribution such that the percentage
20   P by weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm and 0.25µm is as given in the following table:

x (µm)	P (%)
2	at least 88
1	at least 60
0.5	at least 30
0.25	at least 10

3.   A method according to claim 2 and wherein the said coarse fraction, optionally after further processing, has a particle size distribution such that the percentage by weight of particles having a size less than xµm, where x is respectively 2µm, 1µm, 0.5µm and 0.25µm, is as given by the following table:

x (µm)	P (%)
2	at least 89
1	at least 70
0.5	at least 35
0.25	10 to 20

4.   A method according to claim 1, claim 2 or claim 3 and which includes the further step of blending the product inorganic particulate material comprising the said coarse fraction optionally after further processing with at least one other pigment material selected from kaolin, calcium carbonate, calcined kaolin, talc, satin white, titanium dioxide, aluminium trihydrate, amorphous silicas and silicates, zinc oxide, barium sulphate and plastic pigments.

5.   A method according to claim 4 and wherein the product inorganic particulate material is blended with an inorganic particulate material from which the feed inorganic particulate material is obtained.

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6.   A method according to any one of claims 1 to 5 and wherein the said fine fraction is separated for use as a valuable kaolin product.

7.   A method according to any one of claims 1 to 6 and wherein the fine fraction is further sub-classified and at least one sub-fraction thereby produced is separated for use as a valuable kaolin product.

8.   A method according to claim 6 or claim 7 and wherein the fine fraction or a sub-fraction thereof is blended with another kaolin pigment material.

9.   A method according to claim 8 and wherein the said other kaolin pigment material comprises an inorganic particulate material from which the said feed material is obtained or the said coarse fraction or a blend containing one or both of these materials.

10.   A method according to any one of claims 1 to 9 and wherein the or each particle size classifier comprises a scroll type decanter centrifuge.

11.   A method according to any one of claims 1 to 10 and which includes the following steps:

(a)   forming a concentrated aqueous suspension of the feed inorganic particulate material;

(b)   subjecting the concentrated suspension formed in step (a) to mechanical working in the plastic state under conditions such that at least 215kJ of energy per kg of kaolin clay on a dry weight basis are dissipated in the cake;

(c)   optionally grinding the solids contained in the suspension by a media attrition grinding process;

(d)   converting the concentrated suspension worked into a fluid aqueous suspension by a procedure involving diluting with water to produce a diluted suspension;

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(e)   subjecting the diluted suspension formed in step (d) to fractionation in a centrifuge to yield a relatively fine fraction and a relatively coarse fraction under conditions such that it is exposed to an acceleration which is in the range of from 1600g to 6000g, where g is the acceleration due to gravity; and

(f)   recovering at least the relatively coarse fraction product as a dispersed aqueous suspension.

The recovered coarse product may for example have a solids concentration of at least 60% by weight.

12.   A method according to claim 11 and wherein the following step (b) a polyelectrolyte dispersing agent is added to the aqueous suspension.

13.   A method according to claim 12 and wherein the dispersing agent comprises a polyacrylate forming up to 1% by weight based on the dry weight of the inorganic particulate material.

14.   A method according to any one of claims 11 to 13 and wherein the relatively coarse fraction is further treated by one or more further beneficiation steps.

15.   A method according to claim 14 and wherein the further beneficiation comprises bleaching and/or magnetic separation of impurities.

16.   An inorganic particulate material which is a product of the method according to any one of the preceding claims.

17.   An inorganic particulate material according to claim 16 and which is the said coarse fraction and wherein the material has in the fully dispersed state a particle size distribution such that the ratio $d_{50} \div d_{30}$ is less than 1.55, where d_{50} is the size value (in micrometres) smaller than which there are 50% by weight of the particles of the inorganic particulate material

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and d_{30} is the size value (in micrometres) smaller than which there are 30% by weight of the particles of the inorganic particulate material.

18. An inorganic particulate material according to claim 17 and wherein the material has a particle size distribution such that the ratio $d_{50} \div d_{30}$ is less than 1.50.

19. An inorganic particulate material according to claim 17 or claim 18 and wherein the d_{50} value is less than 2µm.

20. An inorganic particulate material according to claim 19 and wherein the d_{50} value is in the range 0.5µm to 1.5µm.

21. An inorganic particulate material according to any one of the preceding claims and wherein at least 90% by weight of the material is kaolin.

22. An inorganic particulate material according to claim 7 and wherein at least 95% by weight of the material is kaolin.

23. An inorganic particulate material according to any one of the preceding claims and having a powder brightness of at least 87 and a powder yellowness of not more than 4.0.

24. An inorganic particulate material according to any one of the preceding claims and which has a particulate shape factor of at least 10.

25. An aqueous paper coating composition comprising a hydrophilic adhesive or binder and a dispersed pigment material wherein the pigment material comprises an inorganic particulate material according to any one of claims 16 to 24 optionally together with one or more other pigment materials.
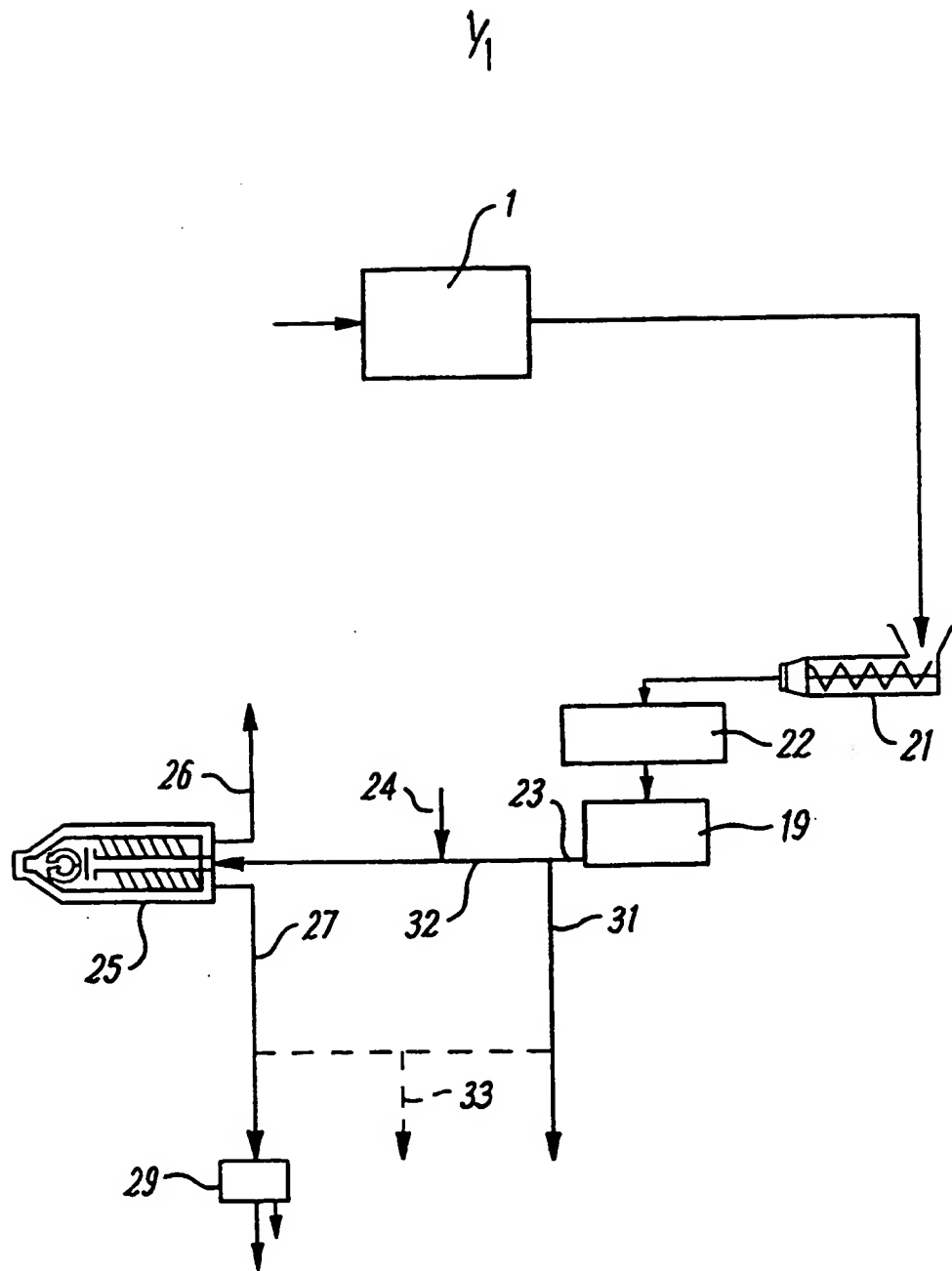
Fig.1

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C09C3/04   C09C1/40   C09C1/42   D21H19/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C09C   D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 169 443 A (WILLIS MITCHELL J ET AL) 8 December 1992 (1992-12-08) the whole document	1,10,11, 25
A	US 5 411 587 A (WILLIS MITCHELL J ET AL) 2 May 1995 (1995-05-02) the whole document	1,11,25
A	EP 0 577 889 A (ECC INT LTD) 12 January 1994 (1994-01-12) the whole document	1,11-14, 25
A	EP 0 396 419 A (ENGELHARD CORP) 7 November 1990 (1990-11-07) the whole document	1-3, 11-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 November 1999	09/11/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340–2040, Tx. 31 651 epo nl, Fax: (+31-70) 340–3016	LIBBERECHT, E

Form PCT/ISA/210 (second sheet) (July 1992)

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